



Yake, A., Corder, T., Moloy, K., Coope, T., Taylor, C., Hung, M., & Pung, S. (2016). Fluorinated Pyridinium and Ammonium Cationic Surfactants. *Journal of Fluorine Chemistry*, 187, 46-55.
<https://doi.org/10.1016/j.jfluchem.2016.05.003>

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Fluorinated Pyridinium and Ammonium Cationic Surfactants

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Abstract

New classes of partially fluorinated cationic surfactants, including pyridinium sulfonates and ammonium hydrochlorides have been prepared in which a fluoroalkyl chain is interrupted either by ether oxygen (-O-), or by methylene (-CH₂-) units. These surfactants are obtained from multi-step syntheses via intermediate fluoroalkyl ethylene iodides (RfO(CF₂CF₂)_nCH₂CH₂I, Rf=C₃F₇, C₂F₅, n=1-3 or Rf(CH₂CF₂)_m(CH₂CH₂)_n, Rf=C₄F₉, C₆F₁₃ m=0-2, n=1-2) or fluoroalkyl iodides (RfI, Rf=C₃F₇O(CF₂CF₂)₃I, C₆F₁₃). The surface activities of these fluorinated cationic surfactants were examined and compared to commercially available fluorinated cationic surfactants used as additives in oil field applications. Some examples demonstrated good performance relative to controls yet are more fluorine efficient because they have lower fluorine content than their perfluoroalkyl analogues. For the ammonium hydrochlorides, the effect of different spacer groups between the cation and the fluorinated chain including ethylene, butylene and isopropylidene on surface activity was also examined.

Keywords:

Fluorosurfactant, Fluorinated pyridinium salt, Fluorinated ammonium hydrochloride, Surface tension, Foaming, Oil field.

1. Introduction

Fluorinated surfactants are a diverse class of surface activity agents. They have a wide variety of applications due to their unique properties such as surface tension reduction, wetting and leveling, exceptional stability in harsh environments (high temperature, high and low pH), hydro- and oleophobicity, etc. They are used as anti-blocking agents in architectural coatings, leveling and wetting agents in paints, inks and floor finishes, aqueous firefighting foams, hard surface cleaners, emulsifiers and dispersion aids for olefin polymerization, and additives in oil and gas extraction fluids [1-9].

In contrast to their hydrocarbon counterparts, fluorinated surfactants often exhibit significantly enhanced performance [8,10]. Hydrocarbon surfactants can generally reduce aqueous surface tension to *ca.* 30 dyne/cm, whereas surface tension reduction as low as 16 dyne/cm can be achieved with fluorosurfactants. Moreover, at the same performance level, the use rate of fluorosurfactants is much lower than that of hydrocarbon surfactants, 0.005-0.1 wt% versus 0.1-3 wt%, respectively. Fluorosurfactants possess outstanding stability in corrosive environments. Fluorosurfactants have been designed to perform in organic, acidic and basic media, while hydrocarbon surfactants are limited to aqueous media. Furthermore the stability of the carbon fluorine bond also enables fluorosurfactants to deliver performance at high temperatures and high pressures.

Fluorinated surfactants are comprised of two key structural components, a hydro- and oleophobic perfluorinated carbon chain (e.g., $\text{F}(\text{CF}_2)_n$), a hydrophilic group, and optionally a spacer separating these two groups. In fluorinated cationic surfactants, the cation is typically a quaternary ammonium group or a protonated amine, including heterocycles [8]. Fluorinated cationic surfactants can be highly effective surface tension reducing and foaming agents in acidic and salt environments. Also, because they are positively charged they can be used to modify negatively charged surfaces. For example, textile surfaces can be

modified with fluorinated cationic surfactants to reduce fiber-fiber, fiber-metal, and fiber-ceramic coefficients of friction [11]. Fluorinated cationic surfactants are additives in aqueous firefighting foams to improve foaming and formulation drainage [8]. They also give improved yields in the emulsion polymerization of olefins [12]. In the case of oil field applications, the oil and gas extraction is conducted in a high temperature, high corrosion environment, and fluorinated cationic surfactants function well in these extraction fluids due to their outstanding thermal and chemical stability [9,13]. In this application, the positively charged surfactant electrostatically absorbs to negatively charged surfaces such as rock fines and sand proppant to reduce capillary forces and improve the recovery of hydrocarbons (oil/gas) and/or the stimulation fluid used to open up the formation. In addition, the cationic surfactant inhibits corrosion by forming a protective film on the metal parts of the well [14].

Fluorinated surfactants are usually more expensive than hydrocarbon surfactants. Although their unique performance attributes offset the added cost to some degree, it is also desirable to increase the fluorine efficiency; i.e., boost the performance of the surfactant so that lesser amounts of the expensive fluorosurfactant are required to achieve the same or better level of performance. It is thus desirable to reduce the chain length of the perfluoroalkyl groups or to reduce the amount of fluorine within a partially fluorinated group, thereby reducing the total fluorine present while still achieving the same or superior surface effects. Additionally, alternative fluorinated materials, including surfactants, with improved environmental properties have been the subject of significant recent attention and review [15-22].

We describe here the syntheses of a few novel fluorinated pyridinium sulfonates and fluorinated ammonium chlorides in which the fluorinated carbon chains are interrupted either by methylene ($-\text{CH}_2$) or ether (e.g., $-\text{O}-$) linkages. We further show that in comparison to their perfluorinated analogues, these interrupted structures are more fluorine efficient with respect to their surface-

active properties. Such a design allows these surfactants to maintain the chemical stability required for harsh application environments, while also translating into reduced cost.

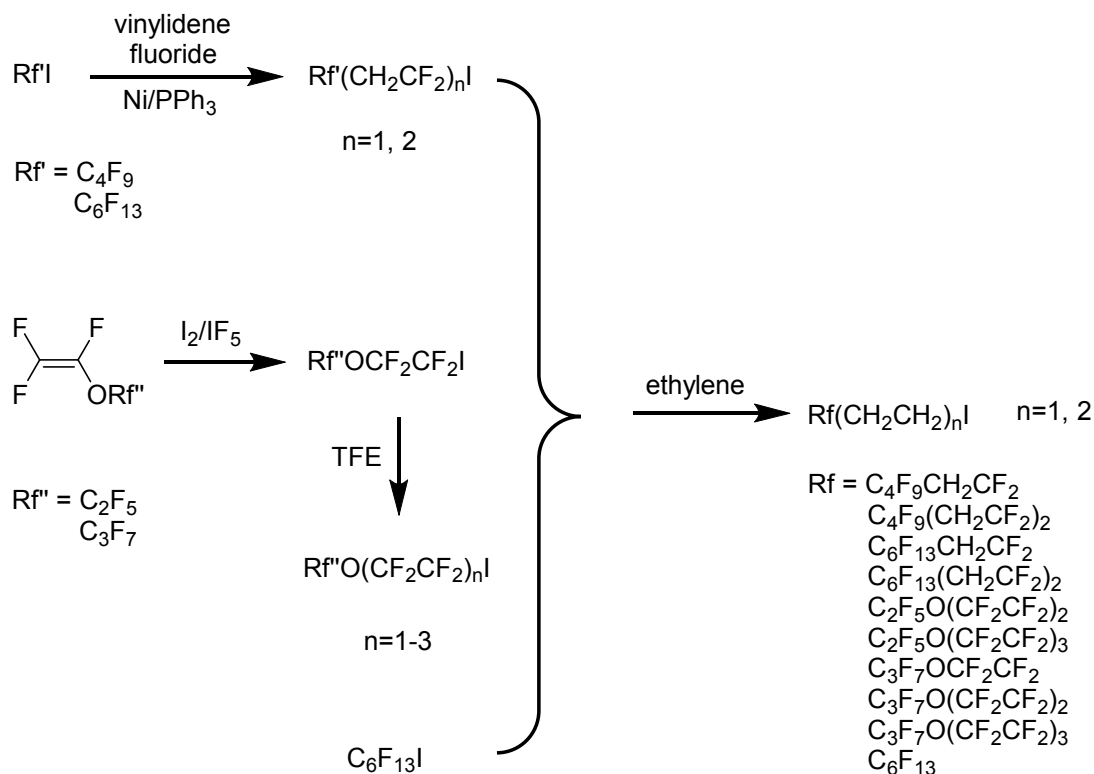
2. Results and Discussion

2.1 Synthesis of Fluoroalkyl Ethylene Iodides

The fluoroalkyl ethylene iodide synthesis is shown in Scheme 1 [23,24]. In the case of fluoroalkyl chains interrupted with methylene groups, the thermal or redox-initiated insertion of vinylidene fluoride (VDF) into fluoroalkyl iodide bonds has been studied extensively by Ameduri and others [25-29]. Here a metal-mediated vinylidene fluoride Insertion of fluoroiodide, followed by radical-mediated ethylene insertion is employed [24]. Access to the fluorinated ethers was accomplished by reaction of perfluorovinyl ether with I_2 and IF_5 to give the fluorinated ether iodides [24], subsequent thermal telomerization with tetrafluoroethylene to extend the chain length, and then insertion of one equivalent of ethylene. The example of a double ethylene insertion in the case of $C_6F_{13}(CH_2CH_2)_2I$ was achieved by reaction of $C_6F_{13}I$ and ethylene in the presence of radical initiator [30]. Fractional distillation was applied in each step for material purification.

Insert Scheme 1

Scheme 1 Synthesis of Fluoroalkyl Ethylene Iodides

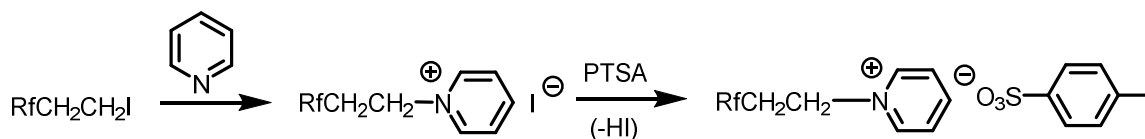


2.2 Synthesis of Fluorinated Pyridinium Surfactants

The fluoroalkyl ethylene iodides were heated with pyridine at 80 °C for 20 hours (Scheme 2). The resulting pyridinium iodide was filtered, washed with ethyl acetate, and dried in the vacuum oven overnight. Yields range from 70 to 95%. Treating this intermediate with *p*-toluene sulfonic acid in methanol at 70 °C for 24-48 hours offered the final product in quantitative yields. In this step methyl iodide and water are generated and constantly removed by distillation to drive the reaction to completion (Scheme 3). These reactions are conveniently followed by periodic gas chromatography of the distillate to monitor the methyl iodide removal. In addition to driving the equilibrium to products, the water stripping may be important to prevent leveling of the acid catalyst and potential inhibition of the reaction rate.

Insert Scheme 2

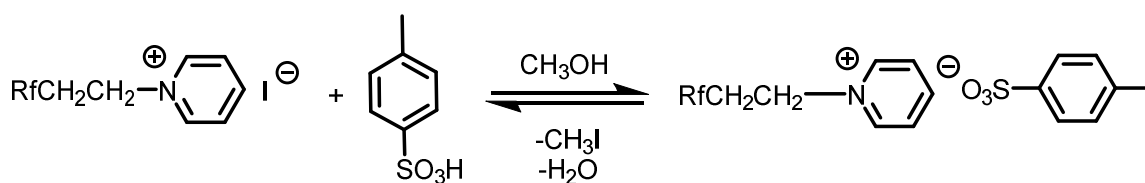
Scheme 2 Synthesis of Fluorinated Pyridinium Surfactants



Rf			
C ₃ F ₇ OCF ₂ CF ₂	I-A	74%	I-B 100%
C ₄ F ₉ CH ₂ CF ₂	II-A	82%	II-B 99%
C ₄ F ₉ (CH ₂ CF ₂) ₂	III-A	86%	III-B 100%
C ₆ F ₁₃ CH ₂ CF ₂	IV-A	93%	IV-B 100%
C ₆ F ₁₃ (CH ₂ CF ₂) ₂	V-A	90%	V-B 100%
C ₆ F ₁₃	VI-A	88%	VI-B 100%

Insert Scheme 3

Scheme 3 Reaction of Fluorinated Pyridinium Iodides with p-Toluene Sulfonic Acid



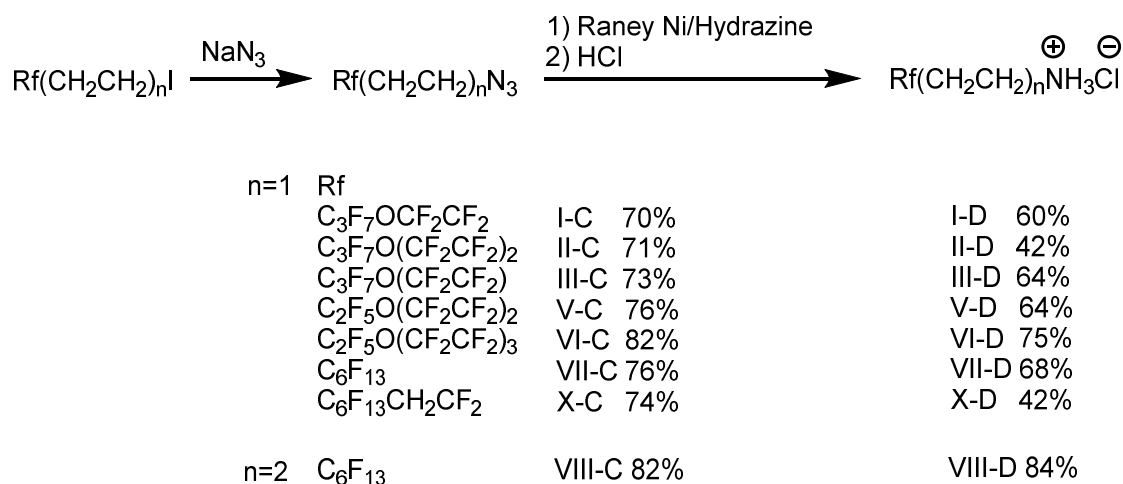
The above fluorinated pyridinium salts were subjected to performance tests as 50 wt% solutions in methanol.

2.3 Synthesis of Fluorinated Ammonium Surfactants

Fluoroalkyl azides with an ethylene spacer were prepared in moderate yields by the biphasic reaction of fluoroalkyl ethylene iodides and sodium azide in the presence tetrabutylammonium bromide as phase transfer catalyst at 100 °C. Raney nickel and hydrazine reduction of the azide intermediates was used to generate the free amines, followed by acidification with HCl to provide the fluoroalkyl ammonium chlorides (Scheme 4).

Insert Scheme 4

Scheme 4 Synthesis of Fluorinated Ethylene Ammonium Surfactants

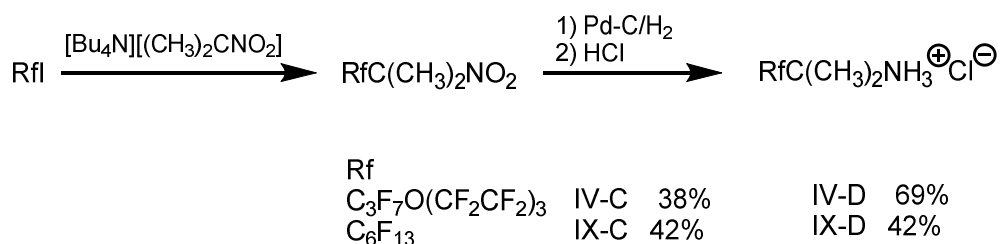


The synthesis of fluoroalkylamines with isopropylidene spacers was first reported by Feiring [31]. The same methodology was applied here to prepare the fluoroether analogues (Scheme 5). Thus, tetrabutylammonium nitropropanide (generated from tetrabutylammonium hydroxide and 2-nitropropane at 85-95 °C) was used to convert C₃F₇O(CF₂CF₂)₃I to C₃F₇O(CF₂CF₂)₃C(CH₃)₂NO₂. This was then reduced to C₃F₇O(CF₂CF₂)₃C(CH₃)₂NH₂ with hydrogen over Pd/C catalyst.

After catalyst removal the amine was purified by distillation. HCl was added to the amine to form the final ammonium chloride salt.

Insert Scheme 5

Scheme 5 Synthesis of Fluorinated Isopropylidene Ammonium Surfactants



2.3 Cationic Fluorosurfactant Performance

2.3.1 Surface Tension

2.3.1.1 Surface Tension in Deionized Water

The fluorinated pyridinium salt and fluorinated ammonium salts described above were diluted into water at different concentrations for surface tension measurement and evaluation (Table 1-2 and Figure 1-3).

Insert Table 1

Insert Figure 1

Table 1 Surface Tensions* (dyne/cm) of Fluorinated Pyridinium Cationic Surfactants in Deionized Water at 23 °C

Surfactants	F (wt %)	Concentration (wt% of surfactant)			
		0.001	0.01	0.1	0.5
[C ₃ F ₇ OCF ₂ CF ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (I-B)	37.1	72.1	64.9	41.0	21.6
[C ₄ F ₉ CH ₂ CF ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (II-B)	37.3	72.1	67.7	43.1	22.8
[C ₄ F ₉ (CH ₂ CF ₂) ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (III-B)	39.5	72.3	59.9	30.5	19.5
[C ₆ F ₁₃ CH ₂ CF ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (IV-B)	43.1	69.5	45.6	18.3	17.2
[C ₆ F ₁₃ (CH ₂ CF ₂) ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (V-B)	44.5	64.2	34.7	18.8	18.3
[RfCH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (Formulation I **)	43.2	68.9	43.0	18.1	17.5
[RfCH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (Formulation II ***)	43.4	67.8	40.6	18.2	17.6
[C ₆ F ₁₃ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (VI-B)	41.4	65.9	51.4	27.5	18.8
[C ₈ F ₁₇ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (Control)	46.3	60.9	30.6	17.2	17.0

* The average of 10 replicates is reported; the standard deviation is <1 dyne/cm

** Formulation I is a mixture of **IV-B** and **V-B** (90:10 mol ratio)

*** Formulation II is a mixture of **IV-B** and **V-B** (80:20 mol ratio)

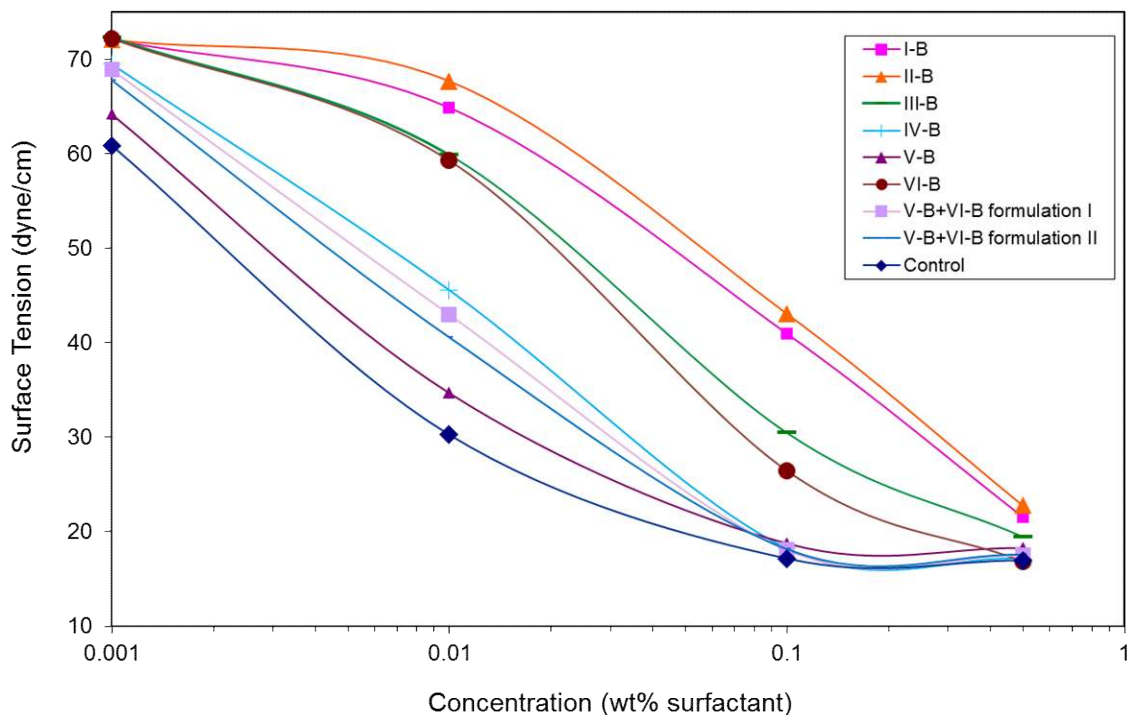


Figure 1 Aqueous Surface Tension of Fluorinated Pyridinium Cationic Surfactants

The surface tension of deionized water is 72 dyne/cm at 23 °C. When the above fluorinated pyridinium cationic surfactants are added at the specified levels, they exhibited different level of surface tension reduction. As shown in Table 1 and Figure 1, surfactants **I-B**, **II-B**, **III-B** and **VI-B** are not as effective as the control example $[n\text{-C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{py}][p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3]$ until reaching concentrations as high as 0.5%. **IV-B** performs equally to the control in the concentration range 0.1-0.5%, but is inferior below 0.1%. **V-B** has the strongest surface tension reduction among all the new surfactants, demonstrating performance only slightly below the control at all tested concentrations. Mixtures of **IV-B** and **V-B** give improved performance over pure **IV-B**, even with only small amounts of **V-B** added.

Insert Table 2

Table 2 Surface Tensions* (dyne/cm) of Fluorinated Ammonium Cationic Surfactants in Deionized Water at 23 °C

Surfactants	F (wt%)	Concentration (wt% of surfactant)			
		0.001	0.01	0.1	0.5
Group I					
[C ₃ F ₇ OCF ₂ CF ₂ CH ₂ CH ₂ NH ₃][Cl] (I-D)	57.2	71.7	68.8	59.1	38.1
[C ₃ F ₇ O(CF ₂ CF ₂) ₂ CH ₂ CH ₂ NH ₃][Cl] (II-D)	61.2	67.2	47.6	25.8	14.3
[C ₃ F ₇ O(CF ₂ CF ₂) ₃ CH ₂ CH ₂ NH ₃][Cl] (III-D)	63.8	52	35.2	16.4	14.8
[C ₃ F ₇ O(CF ₂ CF ₂) ₃ C(CH ₃) ₂ NH ₃][Cl] (IV-D)	62.3	71.2	68.3	54.7	28
[C ₂ F ₅ O(CF ₂ CF ₂) ₂ CH ₂ CH ₂ NH ₃][Cl] (V-D)	59.4	69.7	59.2	36.2	14.6
[C ₂ F ₅ O(CF ₂ CF ₂) ₃ CH ₂ CH ₂ NH ₃][Cl] (VI-D)	62.6	57.3	27.9	16.9	15.5
[RfCH ₂ CH ₂ NH ₃][Cl] (Control**)	65.8	67.1	30.3	23.7	20.9
Group II					
[C ₆ F ₁₃ CH ₂ CH ₂ NH ₃][Cl] (VII-D)	61.8	70.1	64.4	47.8	23.8
[C ₆ F ₁₃ (CH ₂ CH ₂) ₂ NH ₃][Cl] (VIII-D)	57.8	70.9	54.9	33.4	15.1
[C ₆ F ₁₃ C(CH ₃) ₂ NH ₃][Cl] (IX-D)	59.7	71.4	63.9	38.3	18.5
[C ₆ F ₁₃ CH ₂ CF ₂ CH ₂ CH ₂ NH ₃][Cl] (X-D)	61.5	65.7	48.1	29.1	14.9
[RfCH ₂ CH ₂ NH ₃][Cl] (Control**)	65.8	67.1	30.3	23.7	20.9

* The average of 10 replicates is reported; the standard deviation is <1 dyne/cm

** Rf is the mixture of C₈F₁₇ and C₁₀F₂₁ (45:55 mol ratio)

Insert Figure 2

Insert Figure 3

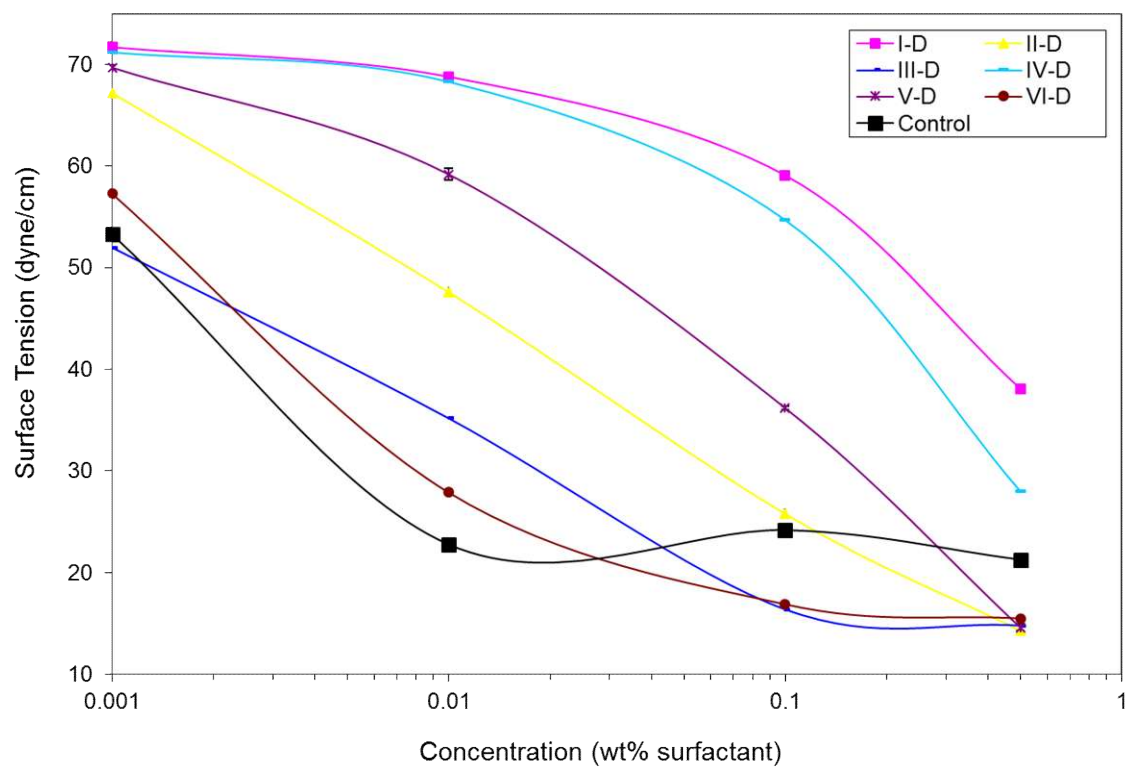


Figure 2 Aqueous Surface Tension of Fluoroether Ammonium Cationic Surfactants (Group I)

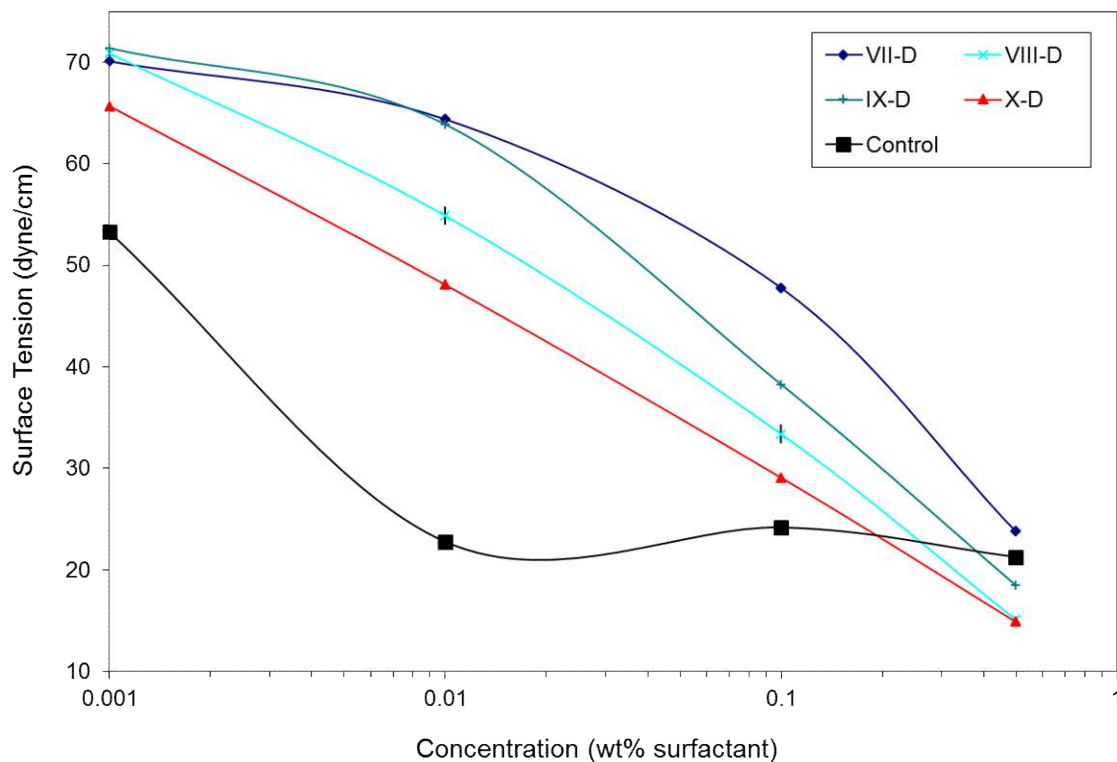


Figure 3 Aqueous Surface Tension of Fluorinated (C_6F_{13}) Ammonium Cationic Surfactants (Group II)

To more closely examine the correlation between surfactant structure and surface tension, the surface tension results of fluorinated ammonium cationic surfactants were divided into two structural groups. Group I ammonium surfactants are a variety of fluoroethers of variable chain length and Group II ammonium surfactants are centered on analogues with different spacers between a fixed, linear C_6F_{13} chain and the ammonium cation. From results shown in Table 2 and Figure 2, in general the surface tension reduction capability of a Group I surfactant is proportional to the fluoroether chain length and the fluorine content. **I-D**, **II-D** and **V-D** show significant performance gaps compared with the control surfactant ($RfCH_2CH_2NH_3[Cl]$, where Rf is a mixture of $n-C_8F_{17}$ and $n-C_{10}F_{21}$). Excellent surface tension reduction is observed with **III-D** and **VI-D**,

which are equal to or better than the control even though both possess lower fluorine content (mass basis). It is worth noting that **III-D** and **IV-D** exhibit dramatic surface activity difference although the only structural difference is the hydrocarbon spacer, ethylene vs. isopropylidene group, respectively. While **III-D** excels in surface tension reduction, **IV-D** shows only moderate performance especially the concentration range 0.001 to 0.1%. There two possible explanations for this phenomenon [32]. The isopropylidene group interrupts the crystalline structure of the surfactant, and thus surfactant **IV-D** does not align or pack well at the liquid-air interface. As a result, the surface tension reduction is not as effective as for **III-D**, which is better able to align/pack. It is also possible that the isopropylidene group diminishes the hydrophilicity of the ammonium ion, thus disrupting the hydrophilic-lipophilic balance.

As indicated in Table II and Figure III, the Group II ammonium surfactants reduce the surface tension of water significantly. Although better performance was obtained at higher concentrations, none of the members of this group of surfactants outperform the control. Given the fixed fluorinated carbon chain (C_6F_{13}), the differences seen among these surfactant are rather interesting. Doubling the alkylidene spacer to butylene in **VIII-D** boosted its surface tension reducing ability relative to the ethylene spacer in **VII-D**. The isopropylidene spacer in **IX-D** provides performance lying between the ethylene and butylene spacers. The best performer in this group is **X-D** in which the spacer is $-CH_2CF_2CH_2CH_2-$. It appears that the dipole provided by difluoromethylene group helps this matter, possibly by enhancing the ability of this surfactant to align and pack at the air-water interface [32].

2.3.3.2 Surface Tension in Aqueous KCl and HCl

Surface tension measurement in 15% HCl and 2% KCl is used to indicate surfactant efficacy in oil well applications. The 2% KCl solution mimics the salinity of the fluids that are used to hydraulically fracture a well. The 15% HCl solution

emulates the acidic stimulation treatment fluids that are used to dissolve the formation rock in wells. At a given concentration, the surfactant with the lower surface tension will help provide improved fluid penetration and recovery for oilfield stimulation fluids [9,33].

The fluorinated pyridinium surfactants were tested for surface tension as 2% KCl aqueous and 15% HCl aqueous solutions as a function of surfactant concentration. These results are summarized in Tables 3-4 and Figures 4-5.

Insert Table 3

Insert Figure 4

Insert Table 4

Insert Figure 5

Table 3 Surface Tensions* (dyne/cm) of Fluorinated Pyridinium Cationic Surfactants in 2% Aqueous KCl at 23 °C

Surfactants	F (wt%)	Concentration (wt% of surfactant)			
		0.001	0.01	0.1	0.5
[C ₃ F ₇ OCF ₂ CF ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (I-B)	37.1	68.5	57.4	40.0	21.8
[C ₄ F ₉ CH ₂ CF ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (II-B)	37.3	54.5	32.2	18.6	17.5
[C ₄ F ₉ (CH ₂ CF ₂) ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (III-B)	39.5	66.5	51.0	28.1	20.0
[C ₆ F ₁₃ CH ₂ CF ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (IV-B)	43.1	54.5	32.2	18.6	17.5
[C ₆ F ₁₃ (CH ₂ CF ₂) ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (V-B)	44.5	42.3	19.4	18.2	17.6
[RfCH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (Formulation I**)	43.2	53.7	28.2	18.3	17.4
[RfCH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (Formulation II***)	43.4	52.8	25.4	18.4	17.7
[C ₆ F ₁₃ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (VI-B)	41.4	65.9	51.4	27.5	18.8
[C ₈ F ₁₇ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (Control)	46.3	41.2	20.1	17.9	17.0

* The average of 10 replicates is reported; the standard deviation is <1 dyne/cm

** Formulation I is a mixture of **IV-B** and **V-B** (90:10 mol ratio)

*** Formulation II is a mixture of **IV-B** and **V-B** (80:20 mol ratio)

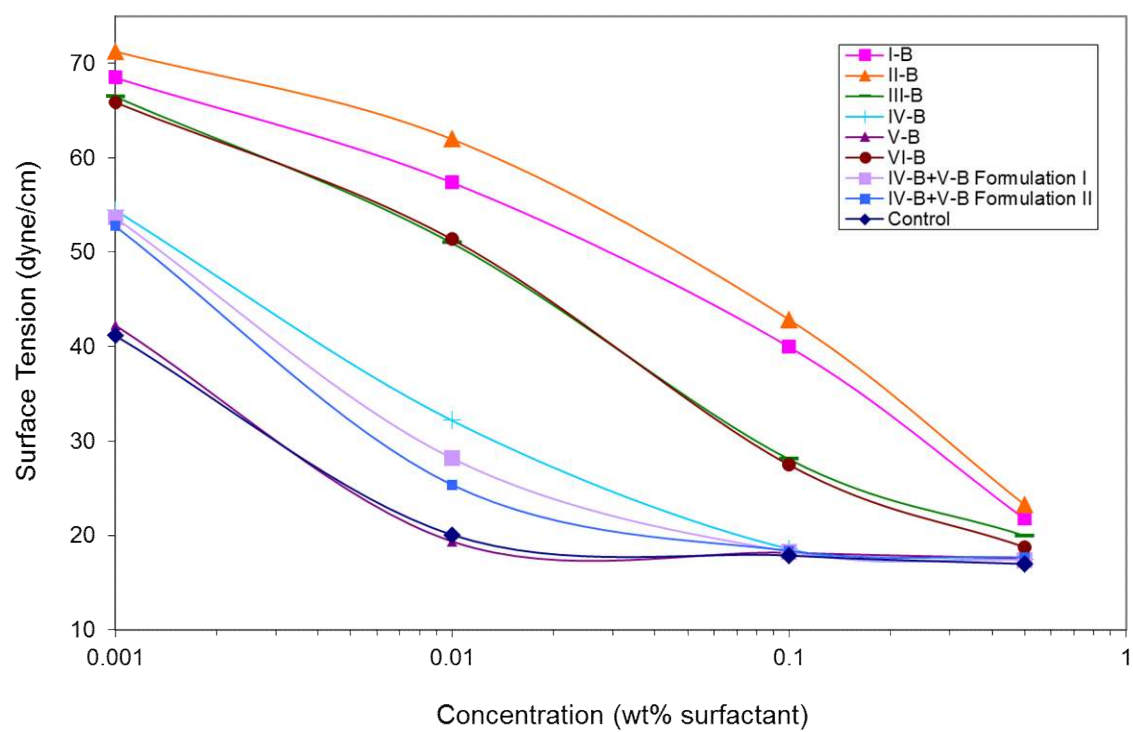


Figure 4 Surface Tensions of Fluorinated Pyridinium Cationic Surfactants in 2% KCl

Table 4 Surface Tensions (dyne/cm) of Fluorinated Pyridinium Cationic Surfactants in 15% Aqueous HCl at 23 °C

Surfactants	F (wt%)	Concentration (wt% of surfactant)			
		0.001	0.01	0.1	0.5
[C ₃ F ₇ OCF ₂ CF ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (I-B)	37.1	67.0	54.8	39.1	25.2
[C ₄ F ₉ CH ₂ CF ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (II-B)	37.3	70.0	60.5	44.4	28.5
[C ₄ F ₉ (CH ₂ CF ₂) ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (III-B)	39.5	65.4	49.1	29.3	22.8
[C ₆ F ₁₃ CH ₂ CF ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (IV-B)	43.1	51.7	29.9	20.0	19.0
[C ₆ F ₁₃ (CH ₂ CF ₂) ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (V-B)	44.5	41.7	19.1	18.6	18.6
[RfCH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (Formulation I**)	43.2	51.5	26.0	19.7	18.9
[RfCH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (Formulation II***)	43.4	50.5	24.4	19.6	18.8
[C ₆ F ₁₃ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (VI-B)	41.4	63.7	47.8	26.8	22.8
[C ₈ F ₁₇ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (Control)	46.3	37.9	19.2	19.2	18.4

* The average of 10 replicates is reported; the standard deviation is <1 dyne/cm

** Formulation I is a mixture of **IV-B** and **V-B** (90:10 mol ratio)

*** Formulation II is a mixture of **IV-B** and **V-B** (80:20 mol ratio)

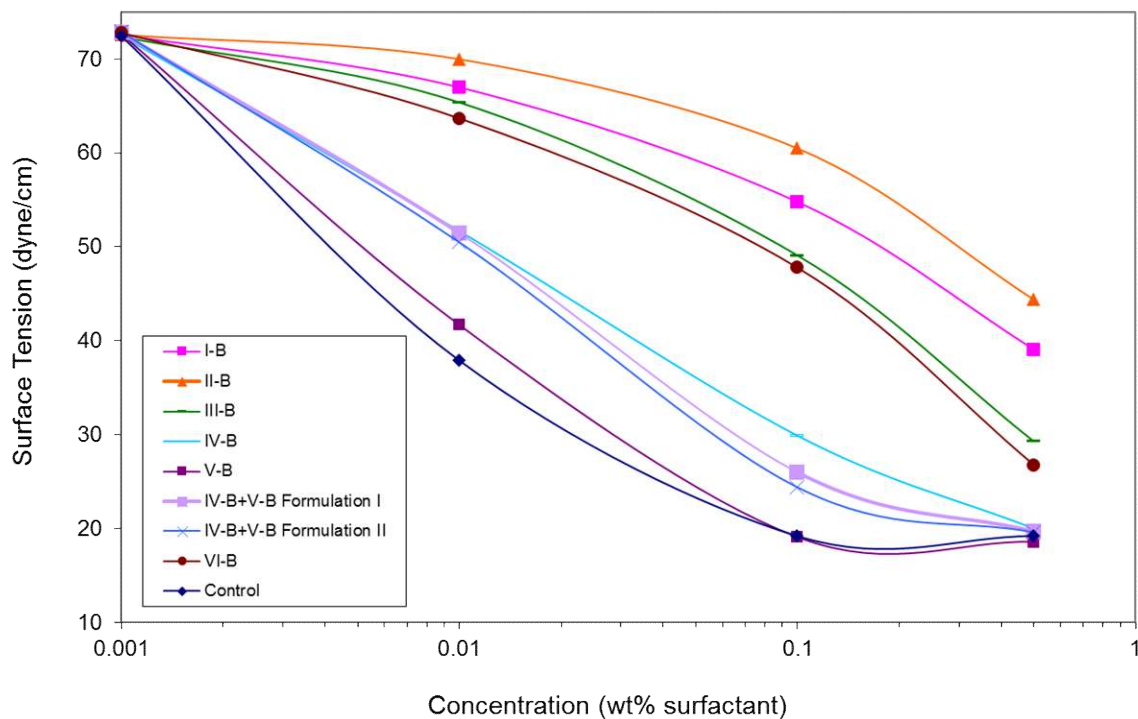


Figure 5 Surface Tensions of Fluorinated Pyridinium Cationic Surfactants in 15% HCl

The normal surface tension of 2% aqueous KCl is 73 dyne/cm and 76 dyne/cm for 15% aqueous HCl. Similarly to their performance in deionized water, these surfactants showed vast performance differences. Compared to the control, poor performance was obtained with **I-B**, **II-B**, **III-B** and **VI-B**. Good surface tension reduction was observed with **IV-B**, and **V-B** performed as well as the control. Again, IVB performance can be improved by formulating 10-20 wt% **V-B** into **IV-B**.

2.3.3 Foaming

Foaming is an essential property of surfactants used as drilling fluid additives as well as for foamed hydraulic fracturing stimulation activities. Foaming during drilling aids in the removal of fines from the well around the drill

bit. If these fines are not efficiently removed, they can cause damage to the drill-bit head, costing time and money [33,34]. The addition of the fluorosurfactant boosts the drilling fluid foaming properties. The cutting bit is lubricated with stable foam which aids in carrying cuttings up to the surface. Lower pressure can be applied to the formulation when using a foam drilling fluid which is particularly important when drilling into low pressure reservoirs. The unique thermal and chemical stability of fluorinated surfactants render them well suited for harsh drilling environments. The use of foams (with surfactants and minimal amounts of water) in hydraulic fracturing allows for reduced water use, treatment, and disposal, by improving the efficacy of the stimulation fluid removal from down hole. The blender foaming test is used as an indicator of the amount of foam that a sample produces as well as the persistence of that foam. The test is also performed in 2% KCl aqueous and 15% HCl aqueous solutions to mimic the stimulation fluid types that are pumped down hole into wells. The test results are listed in Table 5-7.

Insert Table 5

Insert Table 6

Insert Table 7

Table 5 Foaming of Fluorinated Pyridinium Cationic Surfactants in Water

Sample ID	F (wt%)	Foam Volume (mL)				
		Initial	t=30 sec	t = 5 min	t= 10 min	t =15 min
[C ₃ F ₇ OCF ₂ CF ₂ CH ₂ CH ₂ py][p-CH ₃ C ₆ H ₄ SO ₃] (I-B)	37.1	105	0	0	0	0
[C ₄ F ₉ CH ₂ CF ₂ CH ₂ CH ₂ py][p-CH ₃ C ₆ H ₄ SO ₃] (II-B)	37.3	108	0	0	0	0
[C ₄ F ₉ (CH ₂ CF ₂) ₂ CH ₂ CH ₂ py][p-CH ₃ C ₆ H ₄ SO ₃] (III-B)	39.5	105	10	5	0	0
[C ₆ F ₁₃ CH ₂ CF ₂ CH ₂ CH ₂ py][p-CH ₃ C ₆ H ₄ SO ₃] (IV-B)	43.1	100	93	87	77	75
[C ₆ F ₁₃ (CH ₂ CF ₂) ₂ CH ₂ CH ₂ py][p-CH ₃ C ₆ H ₄ SO ₃] (V-B)	44.5	106	105	97	91	73
[RfCH ₂ CH ₂ py][p-CH ₃ C ₆ H ₄ SO ₃] (Formulation I ^{**})	43.2	105	97	88	73	65
[RfCH ₂ CH ₂ py][p-CH ₃ C ₆ H ₄ SO ₃] (Formulation II ^{***})	43.4	103	98	84	74	68
[C ₆ F ₁₃ CH ₂ CH ₂ py][p-CH ₃ C ₆ H ₄ SO ₃] (VI-B)	41.4	98	13	7	2	0
[C ₈ F ₁₇ CH ₂ CH ₂ py][p-CH ₃ C ₆ H ₄ SO ₃] (Control)	46.3	106	100	97	86	73

* Sample was added to deionized water by weight based on solids of the additive in methanol to make 100 mL 0.1% solution

** Formulation I is a mixture of IV-B and V-B (90:10 mol ratio)

*** Formulation II is a mixture of IV-B and V-B (80:20 mol ratio)

Table 6 Foaming of Fluorinated Pyridinium Cationic Surfactants in 2% KCl
Aqueous Solution

Sample ID	F (wt%)	Foam Volume (mL)				
		Initial	t=30 sec	t = 5 min	t= 10 min	t =15 min
[C ₃ F ₇ OCF ₂ CF ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (I-B)	37.1	117	0	0	0	0
[C ₄ F ₉ CH ₂ CF ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (II-B)	37.3	110	0	0	0	0
[C ₄ F ₉ (CH ₂ CF ₂) ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (III-B)	39.5	110	71	2	0	0
[C ₆ F ₁₃ CH ₂ CF ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (IV-B)	43.1	110	101	99	88	75
[C ₆ F ₁₃ (CH ₂ CF ₂) ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (V-B)	44.5	106	101	91	71	66
[RfCH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (Formulation I)	43.2	110	102	99	89	78
[RfCH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (Formulation II)	43.4	113	105	101	89	78
[C ₆ F ₁₃ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (VI-B)	41.4	104	44	4	3	3
[C ₈ F ₁₇ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (Control)	46.3	111	101	101	81	76

* Sample was added to 2% KCl aqueous solution by weight based on solids of the additive in methanol to make 100 mL 0.1% solution

Table 7 Foaming of Fluorinated Pyridinium Cationic Surfactants in 15% HCl
Aqueous Solution

Sample ID	F (wt%)	Foam Volume (mL)				
		Initial	t=30 sec	t = 5 min	t= 10 min	t =15 min
[C ₃ F ₇ OCF ₂ CF ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (I-B)	37.1	112	1	0	0	0
[C ₄ F ₉ CH ₂ CF ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (II-B)	37.3	111	0	0	0	0
[C ₄ F ₉ (CH ₂ CF ₂) ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (III-B)	39.5	117	102	41	21	11
[C ₆ F ₁₃ CH ₂ CF ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (IV-B)	43.1	118	105	101	99	99
[C ₆ F ₁₃ (CH ₂ CF ₂) ₂ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (V-B)	44.5	116	107	106	106	106
[RfCH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (Formulation I)	43.2	114	108	106	106	106
[RfCH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (Formulation II)	43.4	108	102	101	101	101
[C ₆ F ₁₃ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (VI-B)	41.4	118	103	48	28	19
[C ₈ F ₁₇ CH ₂ CH ₂ py][<i>p</i> -CH ₃ C ₆ H ₄ SO ₃] (Control)	46.3	116	106	106	106	106

* Sample was added to 15% HCl aqueous solution by weight based on solids of the additive in methanol to make 100 mL 0.1% solution

The foaming tests follow the trends observed in the surface tension studies. Thus, **I-B**, **II-B** and **III-B** did not provide persistent, stable foams in the test. **V-D** showed equal performance to the control. **IV-D** performance was between **VI-D** and **V-D**, and improvement can be obtained by formulating a small percentage of **V-D** into **IV-D**. Overall **V-D**, Formulation I, and Formulation II demonstrated comparable performance to the control. From a practical point of view, using a mixture of **IV-D** and **V-D** is cost beneficial as these are coproducts

resulting from the insertion of vinylidene fluoride into 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-6-iodohexane.

3. Conclusions

Fluorinated pyridinium and ammonium cationic surfactants have been prepared in moderate to good yields, where the organofluorinated chain is interrupted with methylene or ether oxygen groups and the hydrocarbon spacer is ethylene, butylene or isopropylidene. These novel fluorosurfactants have lower fluorine content (wt% basis) and therefore are more fluorine efficient than their perfluoroalkyl analogues. Aqueous surface tension and foaming of these new fluorinated cationic surfactants were tested.

4. Experimental

4.1 General

Nonfluorinated starting materials and solvents were obtained from Sigma-Aldrich Inc., St. Louis, MO, EMD Chemicals Inc. (Merck KGaA, Darmstadt, Germany) and Alfa Aesar, Ward Hill, MA. Perfluoroalkyl iodides, perfluorovinyl ether, vinylidene fluoride, tetrafluoroethylene, and iodine pentafluoride were from E. I. du Pont de Nemours. All reagents were used without further purification.

Nuclear magnetic resonance spectra of hydrogen nuclei were recorded using a Bruker Avance DRX® (400 MHz) and fluorine-19 nuclei using a Bruker Avance DRX® (376 MHz). Abbreviations for coupling patterns are as follows: s (singlet), d (doublet), t (triplet), tt (triplet of triplets), q (quartet), quin (quintet) and m (multiplet). Elemental analysis was performed by Micro Analysis Inc., Wilmington, DE 19808. Mass spectra (MS) were obtained using an Agilent Technologies 5973 Network mass selective detector coupled to an Agilent Technologies 6890N Network GC System. In this document: F wt% is the weight percentage of fluorine in the pure active ingredient.

4.2 Performance Test Methods

4.2.1 Surface tension was measured according to the American Society for Testing and Materials ASTM D1331-56, using the Wilhelmy plate method on a KRUSS K11 Version 2.501 tensiometer (KRUSS USA, Matthews NC) in accordance with the vendor-provided instructions. A vertical plate of known perimeter was attached to a balance, and the force due to wetting was measured. Ten replicates were tested at each surfactant concentration, and the following machine settings were used:

Method: Plate Method SFT

Interval: 1.0 s

Wetted length: 40.2mm

Reading limit: 10

Min Standard Deviation: 2 dynes/cm

Gr. Acc.: 9.80665 m/s²

Results are reported in dynes/cm (mN/m) and standard deviations were less than 1 dyne/cm.

A stock solution is prepared for the highest concentration of fluorosurfactant to be analyzed. The concentration of the solution is by percent active ingredient, based on either weight percentage or fluorine content. This stock solution is prepared in de-ionized water, 2% KCl, or 15% HCl depending on the desired application for which the surface tension is being measured. The stock solution is stirred overnight (for approximately 12 hours) to ensure complete mixing. Additional concentrations of the fluorosurfactant for analysis are made by diluting the stock solution. The diluted samples are shaken thoroughly and then left undisturbed for 30 minutes. These samples are then remixed and subjected to the analysis with the Krus 11 Tensiometer.

4.2.2 A modified version of ASTM D3519-88 was used to quantify foaming performance. A blender, graduated cylinder, glass sample bottles and a stop watch were employed. Samples (100 mL) of the fluorosurfactant at 0.1 wt% concentration were prepared in deionized water, 2% KCl, and 15% HCl and stirred overnight to ensure complete mixing. The blender was rinsed with deionized water, then acetone, and then de-ionized water again. The test fluid sample was added to the blender jar and the temperature recorded. The blender was then run for 20 seconds at 50-60% power. After 20 seconds, the liquid and foam were immediately poured into a 500 mL graduated cylinder. The initial liquid and foam heights were measured immediately and then again at 5, 10 and 15 min intervals. During this time, any observations of the foam such as its density or persistency were recorded. The variability in these foam height data is 10 mL.

4.3 Fluoroalkyl ethyl iodides $RfCH_2CH_2I$ ($Rf=C_4F_9CH_2CF_2$, $C_4F_9(CH_2CF_2)_2$, $C_6F_{13}CH_2CF_2$, $C_6F_{13}(CH_2CF_2)_2$, $C_6F_{13}(CH_2CH_2)_2I$ and $C_3F_7OCF_2CF_2CH_2CH_2I$) were prepared according to literature methods[23,24,30].

4.4 Synthesis of 1,1,2,2,3,3,4,4-octafluoro-1-iodo-4-(heptafluoropropoxy)butane $C_3F_7OCF_2CF_2CF_2CF_2I$ and 1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-1-iodo-6-(heptafluoropropoxy)hexane $C_3F_7OCF_2CF_2CF_2CF_2CF_2CF_2I$

Tetrafluoroethylene (180 g, 1.8 mol) was introduced to an autoclave charged with $C_3F_7OCF_2CF_2I$ (600 g, 1.46 mol), and the reactor was heated at 230 °C for 2 h. The reaction was repeated two more times. The products were combined and isolated by vacuum distillation to provide $C_3F_7OCF_2CF_2CF_2CF_2I$ (370 g, 29%) and $C_3F_7OCF_2CF_2CF_2CF_2CF_2CF_2I$ (234 g, 18%) based on recovered starting material. $C_3F_7OCF_2CF_2CF_2CF_2I$: b.p. 63-66 °C at 60 mmHg; ^{19}F NMR ($CDCl_3$, 376 MHz): δ -65.63 - -65.75 (2F, m), -82.65 (3F, t, $J=7.3$ Hz), -84.41 - -84.54 (2F, m), -85.34 - -85.47 (2F, m), -115.07 (2F, s), -125.49 - -125.61 (2F, m), -131.03 (2F, s); MS (PCI): 513(M^++1); $C_7F_{15}OI$ (511.88); Calc. C 16.41 F 55.67; Found C 16.57 F 56.95. $C_3F_7OCF_2CF_2CF_2CF_2CF_2CF_2I$: ^{19}F NMR ($CDCl_3$,

376 MHz): δ -65.33 -65.45 (2F, m), -82.72 (3F, t, $J=7.2$ Hz), -84.08 - 84.21 (2F, m), -85.37 - 85.47 (2F, m), -114.60 - 114.75 (2F, m), -121.96 - - 122.18 (2F, m), - 123.19 (2F, s), -126.43- -126.55 (2F, m), -131.09 (2F, s); MS (PCI): 613(M^++1); $C_{11}F_{19}OI$ (611.87) Calc. C 17.65 F 59.00; Found C 17.76 F 57.62.

4.5 Synthesis of 1,1,2,2,3,3,4,4-octafluoro-6-iodo-1-(heptafluoropropoxy)hexane $C_3F_7OCF_2CF_2CF_2CF_2CH_2CH_2I$ and 1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-8-iodo-1-(heptafluoropropoxy)octane $C_3F_7OCF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2I$

Ethylene (12 g, 0.4 mol) was introduced to an autoclave charged with $C_3F_7OCF_2CF_2CF_2CF_2I$ (177 g, 0.33 mol). The reactor was then heated at 220 °C for 12 hours. The product $C_3F_7OCF_2CF_2CF_2CF_2CH_2CH_2I$ was purified via vacuum distillation (115 g, 65% yield). b.p. 68-71 °C at 14.5 mmHg; 1H NMR ($CDCl_3$, 400 MHz) δ 3.16 (2H, t, $J = 7.9$ Hz), 2.70-2.55 (2H, m); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -82.22 (3F, t, $J = 7.4$ Hz), -83.98 - -84.15 (2F, m), -85.02 - -85.18 (2F, m), -115.81- -116.01 (2F, m), -124.45 - -124.61 (2F, m), -123.03 - -123.17 (2F, m), -130.71 - -130.74 (2F, m); MS (PCI): 542 (M^++1); $C_9H_4F_{15}OI$ (540.00) Calc. C 20.02 H 0.75 F 55.67 Found C 20.18 H 0.63 F 56.95.

Ethylene (41.0 g, 1.46 mol) was introduced to an autoclave charged with $C_3F_7OCF_2CF_2CF_2CF_2CF_2CF_2I$ (500 g, 0.82 mol). The reactor was then heated at 220 °C for 12 hours. The product $C_3F_7OCF_2CF_2CF_2CF_2CF_2CF_2CH_2CH_2I$ was purified via vacuum distillation (311.53 g, 60% yield). b.p. 95-97 °C at 13 mmHg; 1H NMR ($CDCl_3$, 400 MHz) δ 3.24 (2H, t-t, $^1J = 8.3$ Hz, $^2J = 2.0$ Hz), 2.78 - 2.63 (2H, m); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -82.51 (3F, t, $J = 7.2$ Hz), -83.92 - -84.07 (2F, m), -85.19 - -85.34 (2F, m), -115.75 - -115.97 (2F, m), -122.56 - -122.82 (2F, m), -123.06 - -123.30 (2F, m), -124.16 - -124.36 (2F, m), -126.29 - -126.46 (2F, m), -130.93 - -130.96 (2F, m); MS (PCI): 640 (M^+); $C_{11}H_4F_{19}OI$ (639.90) Calc. C 20.63; H 0.63 F 56.41; Found C 20.83 H 0.62 F 59.42.

4.6 Synthesis of 1-(3,3,4,4-tetrafluoro-4-(heptafluoropropoxy)butyl)pyridin-1-ium iodide [$\text{C}_3\text{F}_7\text{OCF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{py}$][I] (**I-A**)

A 100 mL, three-neck round bottom flask was charged with $\text{C}_3\text{F}_7\text{OCF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ (20.0 g, 0.0455 mol) and pyridine (17.4 g, 0.222 mol) under nitrogen. The reaction was allowed to reflux at 80 °C for 20 hours. The reaction mixture was cooled to room temperature before isolating the off-white solid product in a fritted funnel. The solid was washed with ethyl acetate (3 x 60 mL), and dried under vacuum overnight to give 17.52 g (74%) of [$\text{C}_3\text{F}_7\text{OCF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{py}$][I] (**I-A**). m.p. 167 – 175 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 9.4 (2H, d, J = 5.9 Hz), 8.45 (1H, t-t, 1J = 1.3 Hz, 2J = 7.9 Hz), 8.13 (2H, t, J = 7.2 Hz), 5.52 (2H, t, J = 6.2 Hz), 3.01 (2H, t-t, 1J = 17.8 Hz, 2J = 6.2 Hz); ^{19}F NMR (CDCl_3 , 376 MHz) δ -83.58 (3F, t, J = 7.4 Hz), -84.66--84.81 (2F, m), -87.62 - -87.72 (2F, m), -116.70 - -116.82 (2F, t, J = 18.2 Hz), -130.10 - -130.13 (2F, m); $\text{C}_{12}\text{F}_{11}\text{ONI}$ (519.09) Calc. C 27.77 H 1.75 F 40.26; Found C 27.46 H 1.65 F 38.63.

The synthesis of compound **II-A** to **V-A** were performed in a similar manner and the experimental details can be found in supplementary data.

4.7 1-(3,3,5,5,6,6,7,7,8,8,8-undecafluorooctyl)pyridin-1-ium iodide [$\text{C}_4\text{F}_9\text{CH}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{py}$][I] (**II-A**) m.p. 174 - 185 °C ^1H NMR (D_2O , 400 MHz) δ 8.95 (2H, d, J = 6.0 Hz), 8.60 (1H, t, J = 7.8 Hz), 8.11 (2H, t, J = 7.0 Hz), 4.96 (2H, t, J = 6.9 Hz), 3.16 (2H, quintet, J = 17.1 Hz), 2.93 (2H, t-t, 1J = 17.7 Hz, 2J = 6.9 Hz); ^{19}F NMR (D_2O , 376 MHz) δ -81.45 (3F, t, J = 9.6 Hz), -95.24 - -95.50 (2F, m), -112.67 - -112.97 (2F, m), -124.90 - -125.02 (2F, m), -126.15 - -126.30 (2F, m); $\text{C}_{13}\text{H}_{11}\text{F}_{11}\text{NI}$ (517.11) Calc. C 30.19 H 2.13 F 40.42. Found C 30.07 H 1.93 F 39.89.

4.8 1-(3,3,5,5,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)pyridin-1-ium iodide [$\text{C}_4\text{F}_9(\text{CH}_2\text{CF}_2)_2\text{CH}_2\text{CH}_2\text{py}$][I] (**III-A**) m.p. 131 -133 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 9.48 (2H, d, J = 6.1 Hz), 8.51 (1H, t, J = 8.1 Hz), 8.09 (2H, t, J = 6.76 Hz), 5.36

(2H, t, J = 6.4 Hz), 3.09 - 2.96 (2H, t-t, 1J = 17.5 Hz, 2J = 6.4 Hz), 2.95 - 2.77 (4H, m); ^{19}F NMR (CDCl_3 , 376 MHz) δ -81.46 (3F, t-t, 1J = 9.7 Hz, 2J = 3.2 Hz), -90.04 - -90.31 (2F, m), -93.92 - -94.17 (2F, m), -112.76 - -112.99 (2F, m), -124.61 - -124.74 (2F, m), -126.16 - -126.29 (2F, m); $\text{C}_{15}\text{H}_{13}\text{F}_{13}\text{NI}$ (581.15) Calc. C 31.00 H 2.25 F 42.50; Found C 30.81 H 2.06 F 41.41.

4.9 1-(3,3,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodecyl)pyridin-1-ium iodide [$\text{C}_6\text{F}_{13}\text{CH}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{py}$][I] (**IV-A**) m.p.: 188 - 193 °C; ^1H NMR (DMSO-d_6 , 400 MHz) δ 9.17 (2H, d, J = 6.2 Hz), 8.65 (1H, t-t, 1J = 7.8 Hz, 2J = 1.3 Hz), 8.21 (2H, t, J = 7.0 Hz), 4.92 (2H, t, J = 7.2 Hz), 3.47 - 3.28 (2H, m), 2.50 (2H, t-t, 1J = 17.7 Hz, 2J = 6.9 Hz); ^{19}F NMR (DMSO-d_6 , 376 MHz) δ -80.67 (3F, t, J = 9.8 Hz), -95.38 - -95.59 (2F, m), -111.58 - -111.80 (2F, m), -121.86 - -122.10 (2F, m), -122.90 - -123.14 (2F, s), -123.19 - -123.40 (2F, m), -126.05 - -126.24 (2F, m); $\text{C}_{15}\text{H}_{11}\text{F}_{15}\text{NI}$ (617.13) Calc. C 29.19 H 1.80 F 46.18; Found C 29.00 H 1.66 F 47.34.

4.10 1-(3,3,5,5,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecyl)pyridin-1-ium iodide [$\text{C}_6\text{F}_{13}(\text{CH}_2\text{CF}_2)_2\text{CH}_2\text{CH}_2\text{py}$][I] (**V-A**) m.p. 138 -145 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 9.49 (2H, d, J = 5.8 Hz), 8.50 (1H, t, J = 7.7 Hz), 8.09 (2H, t, J = 7.1 Hz), 4.93 (2H, t, J = 6.3 Hz), 3.03 (2H, t-t, 1J = 17.6 Hz, 2J = 6.5 Hz), 2.95 - 2.76 (4H, m); ^{19}F NMR (CDCl_3 , 376 MHz) δ -81.19(3F, t-t, 1J = 9.9 Hz, 2J = 2.2), -89.83 - -90.04 (2F, m), -94.10 - -94.30 (2F, m), -112.54 - -112.74 (2F, m), -121.96 - -122.18 (2F, m), -123.09 - -123.27 (2F, m), -123.65 - -123.81 (2F, m), -126.41 - -126.54 (2F, m); $\text{C}_{17}\text{H}_{13}\text{F}_{17}\text{NI}$ (680.98) Calc. C 29.96 H 1.92 F 47.43; Found C 30.02 H 1.73 F 47.89.

4.11 Synthesis of 1-(3,3,4,4-tetrafluoro-4-(heptafluoropropoxy)butyl)pyridin-1-ium 4-methylbenzenesulfonate [$\text{C}_3\text{F}_7\text{OCF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{py}$][*p*- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3$] (**I-B**)

A 100 mL, three-neck round bottom flask equipped with a distillation column was charged with [$\text{C}_3\text{F}_7\text{OCF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{py}$][I] (10.0 g, 0.019 mol) and

methanol (6.4 g, 0.20 mol) under nitrogen and heated to 60 °C. A solution of p-toluenesulfonic acid (4.28 g, 0.023 mol) in methanol (4.0 g, 0.122 mol) was added dropwise into the reaction flask. The reaction was heated to 60 °C for 76 hours (until CH₃I could no longer be detected by GC in the distillate), while additional methanol was added periodically to replenish the distilled solvent. Methanol was then evaporated off to yield [C₃F₇OCF₂CF₂CH₂CH₂py][p-CH₃C₆H₄SO₃] as a beige solid (10.84 g, 100%). The product was then dissolved in methanol to obtain a 50% solution, and neutralized to a pH of 5.5 ± 0.5 with 3.5% NaOH aqueous solution. ¹H NMR (CDCl₃, 400 MHz) δ 9.20 (2H, d, J = 5.9 Hz), 8.46 (1H, t, J = 7.8 Hz), 8.06 (2H, t, J = 7.3 Hz), 7.70 (2H, d, J = 8.2 Hz), 7.17 (2H, d, J = 8.1 Hz), 5.22 (2H, t, J = 6.4 Hz), 2.93 (2H, t-t, ¹J = 18.2 Hz, ²J = 6.2 Hz), 2.35 (3H, s); ¹⁹F NMR (CDCl₃, 376 MHz) δ -81.73 (3F, t, J = 7.5 Hz), -84.80 - -84.96 (2F, m), - 87.83 - -87.95 (2F, m), -117.37 (2F, t, J = 18.3 Hz), -130.25 - -130.29 (2F, m).

The synthesis and formulation of compound **II-B** to **VI-B** were performed in a similar manner and the experimental details can be found in supplementary data.

4.12 1-(3,3,5,5,6,6,7,7,8,8,8-undecafluorooctyl)pyridin-1-ium 4-methylbenzenesulfonate [C₄F₉CH₂CF₂CH₂CH₂py][p-CH₃C₆H₄SO₃] (**II-B**) ¹H NMR (CDCl₃, 400 MHz) δ 9.20 (2H, d, J = 5.6 Hz), 8.43 (1H, t, J = 8.0 Hz), 8.03 (2H, t, J = 8.0 Hz), 7.70 (2H, t, J = 8.2 Hz), 7.16 (2H, d, J = 8.0 Hz), 5.11 (2H, t, J = 6.2 Hz), 3.01-2.76 (4H, m), 2.33 (3H, s); ¹⁹F NMR (CDCl₃, 376 MHz) δ -81.58 (3F, t-t, ¹J = 9.8 Hz, ²J = 2.6 Hz), -94.82 - -95.09 (2F, m), -112.80 - -113.10 (2F, m), -124.60 - -124.78 (2F, m), -126.28 - -126.44 (2F, m)

4.13 1-(3,3,5,5,6,6,7,7,8,8,8-undecafluorooctyl)pyridin-1-ium 4-methylbenzenesulfonate [C₄F₉(CH₂CF₂)₂CH₂CH₂py][CH₃C₆H₄SO₃] (**III-B**) ¹H NMR (CDCl₃, 400 MHz) δ 9.28 (2H, d, J = 6.0 Hz), 8.31 (1H, t, J = 7.8 Hz), 7.89 (2H, t, J = 7.3 Hz), 7.67 (2H, d, J = 8.1 Hz), 7.12 (2H, d, J = 8.1 Hz), 5.10 (2H, t, J

= 6.6 Hz), 2.90 - 2.71 (6H, m), 2.30 (3H, s); ^{19}F NMR (CDCl_3 , 376 MHz) δ -81.59 (3F, t-t, 1J = 9.9 Hz, 2J = 3.7 Hz), -91.07 - -91.31 (2F, m), -94.26 - -94.50 (2F, m), -112.79 - -113.10 (2F, s), -124.63 - -124.86 (2F, m), -126.25 - -126.50 (2F, m).

4.14 1-(3,3,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodecyl)pyridin-1-ium 4-methylbenzenesulfonate $[\text{C}_6\text{F}_{13}\text{CH}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{py}][\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3]$ (**IV-B**) ^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ 9.17 (2H, d, J = 6.3 Hz), 8.64 (1H, t, J = 7.8 Hz), 8.20 (2H, t, J = 7.2 Hz), 7.48 (2H, d, J = 8.2 Hz), 7.10 (2H, d, J = 8.0 Hz), 4.91 (2H, t, J = 6.9 Hz), 3.48 - 3.31 (2H, m), 2.90 (2H, t-t, 1J = 17.6 Hz, 2J = 6.8 Hz), 2.29 (3H, s); ^{19}F NMR ($\text{DMSO}-d_6$, 376 MHz) δ -80.65 (3F, t-t, 1J = 9.6 Hz, 2J = 2.7 Hz), -95.35 - -95.63 (2F, m), -111.46 - -111.85 (2F, m), -121.85 - -122.10 (2F, m), -122.90 - -123.13 (2F, s), -123.19 - -123.39 (2F, m), -126.03 - -126.23 (2F, m).

4.15 1-(3,3,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)pyridin-1-ium 4-methylbenzenesulfonate $[\text{C}_6\text{F}_{13}(\text{CH}_2\text{CF}_2)_2\text{CH}_2\text{CH}_2\text{py}][\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3]$ (**V-B**) ^1H NMR (CDCl_3 , 400 MHz) δ 9.22 (2H, d, J = 5.9 Hz), 8.31 (1H, t, J = 7.9 Hz), 7.92 (2H, t, J = 7.1 Hz), 7.68 (2H, d, J = 8.3 Hz), 7.12 (2H, d, J = 8.0 Hz), 5.11 (2H, t, J = 6.5 Hz), 2.93 - 2.68 (6H, m); ^{19}F NMR (CDCl_3 , 376 MHz) δ -81.30 (3F, t-t, 1J = 9.9 Hz, 2J = 2.2), -90.87 - -91.13 (2F, m), -94.49 - -94.13 (2F, m), -112.53 - -112.87 (2F, m), -122.08 - -122.35 (2F, m), -123.16 - -123.43 (2F, m), -123.66 - -123.91 (2F, m), -126.48 - -126.74 (2F, m).

4.16 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)pyridin-1-ium 4-methylbenzenesulfonate $[\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{py}][\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3]$ (**VI-B**) ^1H NMR (D_2O , 400 MHz) δ 8.87 (2H, d, J = 6.0 Hz), 8.54 (1H, t, J = 8.0 Hz), 8.04 (2H, t, J = 7.2 Hz), 7.68 (2H, d, J = 8.0 Hz), 7.13 (2H, d, J = 8.3 Hz), 4.90 (2H, t, J = 6.9 Hz), 2.95 - 2.76 (2H, m), 2.16 (3H, s); ^{19}F NMR (D_2O , 376 MHz) δ -85.16 - -85.29 (3F, m), -116.09 - -116.80 (2F, m), -124.75 - -125.30 (2F, m), -125.89 - -126.53 (4F, m), -129.55 - -130.10 (2F, m)

4.17 Synthesis of 4-azido-1,1,2,2-tetrafluoro-1-(heptafluoropropoxy)butane
 $\text{C}_3\text{F}_7\text{OCF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{N}_3$ (**I-C**)

Sodium azide (33.2 g, 0.511 mol) was dissolved in 100 mL of water and charged into a three-neck round bottom flask under nitrogen along with tetrabutylammonium bromide (3.3 g, 0.010 mol). $\text{C}_3\text{F}_7\text{OCF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ (150 g, 0.340 mol) was charged into the flask and the reaction was heated to 100 °C for 28 hours. Based on results from GC monitoring, additional NaN_3 was added to the reaction flask (5.0 g, 0.077 mol) to drive the reaction to completion. After 28 hours, the reaction was cooled to room temperature and the organic layer was isolated. NaI was removed from the product through gravity filtration, and the organic layer was washed five times with 100 mL of 60 °C water. Distillation gave 85.17 g (70%) of $\text{C}_3\text{F}_7\text{OCF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{N}_3$ (**I-C**) as a colorless liquid. b.p.: 44 - 45 °C at 10 mmHg; ^1H NMR (CDCl_3 , 400 MHz) δ 3.58 (2H, t, $J = 7.3$ Hz), 2.31 (2H, t-t, $^1J = 17.7$ Hz, $^2J = 7.4$ Hz); ^{19}F NMR (CDCl_3 , 376 MHz) δ -82.00 (3F, t, $J = 7.5$ Hz), -85.10 - -85.26 (2F, m), -85.56 - -85.67 (2F, m), -118.55 (2F, t, $J = 17.5$ Hz), -130.56 - -130.59 (2F, m); $\text{C}_7\text{H}_4\text{F}_{11}\text{ON}_3$ (355.02) Calc. C 23.73 H 1.08; Found C 23.66 H 1.14.

The synthesis of compound **II-C**, **III-C**, **V-C** to **IX-C** were performed in a similar manner and the experimental details can be found in supplementary data.

4.18 6-azido-1,1,2,2,3,3,4,4-octafluoro-1-(heptafluoropropoxy)hexane
 $\text{C}_3\text{F}_7\text{O}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{CH}_2\text{N}_3$ (**II-C**) ^1H NMR (CDCl_3 , 400 MHz) δ 3.57 (2H, t, $J = 7.2$ Hz), 2.35 (2H, t-t, $^1J = 18.2$ Hz, $^2J = 7.2$ Hz); ^{19}F NMR (CDCl_3 , 376 MHz) δ -82.62 (3F, t, $J = 7.4$ Hz), -84.28 - -84.44 (2F, m), -85.31 - -85.47 (2F, m), -115.11 - -115.33 (2H, m), -124.82 - -124.97 (2F, s), -126.25 - -126.40 (2F, m), -131.04 - -131.07 (2H, m); MS (PCI): 456 ($\text{M}^+ + 1$); HRMS Calcd for $\text{C}_9\text{H}_5\text{F}_{15}\text{ON}$ ($\text{M}^+ - \text{N}_2 + \text{H}$): 428.0132 Found: 428.0110.

4.19 8-azido-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-1-(heptafluoropropoxy)octane
 $\text{C}_3\text{F}_7\text{O}(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{N}_3$ (**III-C**) ^1H NMR (CDCl_3 , 400 MHz) δ 3.59 (2H, t, J = 7.3 Hz), 2.37 (2H, t-t, 1J = 18.2 Hz, 2J = 7.3 Hz); ^{19}F NMR (CDCl_3 , 376 MHz) δ - 82.54 (3F, t, J = 6.7 Hz), -83.92 - -84.10 (2F, m), -85.20 - -85.36 (2F, m), -114.78 - -115.02 (2H, m), -122.55 - -122.85 (2F, m), -123.06 - -123.30 (2H, m), -124.31 - -124.50 (2H, m), -126.27 - -126.48 (2F, m), -130.34 - -130.99 (2H, m); MS (PCI): 556 ($M^+ + 1$); $\text{C}_{11}\text{H}_4\text{F}_{19}\text{ON}_3$ (555.13) Calc. C 23.93 H 0.65; Found C 23.80 H 0.73.

4.20 6-azido-1,1,2,2,3,3,4,4-octafluoro-1-(pentafluoroethoxy)hexane
 $\text{C}_2\text{F}_5\text{O}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{CH}_2\text{N}_3$ (**V-C**) ^1H NMR (CDCl_3 , 400 MHz) δ 3.59 (2H, t, J = 7.1 Hz), 2.37 (2H, t-t, 1J = 18.3 Hz, 2J = 7.3 Hz); ^{19}F NMR (CDCl_3 , 376 MHz) δ - 84.07 - -84.24 (2F, m), -87.63 - -87.66 (3F, t), -89.13 - -89.23 (2F, m), -114.73 - -114.96 (2H, m), -124.52 - -124.65 (2F, s), -125.97 - -126.11 (2F, m); MS (PCI): 406 ($M^+ + 1$); $\text{C}_8\text{H}_4\text{F}_{13}\text{ON}_3$ (405.11) Calc. C 23.86 H 0.87. Found C 23.72 H 1.00.

4.21 8-azido-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-1-(pentafluoroethoxy)octane
 $\text{C}_2\text{F}_5\text{O}(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{N}_3$ (**VI-C**) ^1H NMR (CDCl_3 , 400 MHz) δ 3.59 (2H, t, J = 7.1 Hz), 2.37 (2H, t-t, 1J = 18.2 Hz, 2J = 7.2 Hz); ^{19}F NMR (CDCl_3 , 376 MHz) δ - 84.04 - -84.20 (2F, m), -87.97 - -88.00 (3F, m), -89.36 - -89.47 (2F, m), -114.75 - -114.97 (2F, m), -122.51 - -122.76 (2H, m), -123.05 - -123.25 (2F, s), -124.27 - -124.47 (2F, m), -126.31 - -126.47 (2H, m); MS (PCI): 506 ($M^+ + 1$); $\text{C}_{10}\text{H}_4\text{F}_{17}\text{ON}_3$ (505.13) Calc. C 24.14 H 0.68; Found C 23.78 H 0.80.

4.22 10-azido-1,1,1,2,2,3,3,4,4,5,5,6,6,8,8-pentadecafluorodecane
 $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{N}_3$ (**VII-C**) b.p. 59 - 61 °C @ 10 mmHg; ^1H NMR (CDCl_3 , 400 MHz) δ 3.60 (2H, t, J = 7.2 Hz), 2.38 (2H, t-t, 1J = 18.3 Hz, 2J = 7.2 Hz); ^{19}F NMR (D_2O , 376 MHz) δ -81.80 (3F, t-t, 1J = 10.0 Hz, 2J = 2.4 Hz), -114.58 - -114.81 (2F, m), -122.44 - -122.73 (2F, m), -123.45 - -123.69 (2F, m), -124.27 (2F, s), -126.83 - -127.07 (2F, m); MS (PCI): 390 ($M^+ + 1$); $\text{C}_8\text{F}_{13}\text{H}_4\text{N}_3$ (389.12); Calc. C 24.60 H 1.01 Found C 24.69 H 1.04; The NMR results are consistent with literature reported value[35].

4.23 12-azido-1,1,1,2,2,3,3,4,4,5,5,6,6,8,8-pentadecafluorododecane
 $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}_3$ (**VIII-C**) ^1H NMR (CDCl_3 , 400 MHz) δ 3.32 (2H, t, J = 6.3 Hz), 2.16 - 2.01 (2H, m), 1.76 - 1.62 (4H, m); ^{19}F NMR (CDCl_3 , 376 MHz) δ -82.02 (3F, t, J = 10.0 Hz), -115.20 - -115.44 (2F, m), -122.58 - -122.86 (2F, m), -123.58 - -123.86 (2F, m), -124.29 - -124.54 (2F, m), -126.99 - -127.18 (2F, m); MS (PCI): 418 ($\text{M}^+ + 1$); $\text{C}_{10}\text{F}_{13}\text{H}_8\text{N}_3$ (417.17) Calc. C 29.52 H 1.81 Found C 28.79 H 1.93; HRMS Calcd for $\text{C}_{10}\text{F}_{13}\text{H}_9\text{N}$ ($\text{M}^+ - \text{N}_2 + \text{H}$) 390.0528; Found 390.0509.

4.24 10-azido-1,1,1,2,2,3,3,4,4,5,5,6,6,8,8-pentadecafluorodecane
 $\text{C}_6\text{F}_{13}\text{CH}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{N}_3$ (**IX-C**) ^1H NMR (CDCl_3 , 400 MHz) δ 3.55 (2H, t, J = 6.9 Hz), 2.85 - 2.67 (2H, m), 2.30 (2H, t-t, 1J = 16.8 Hz, 2J = 7.2 Hz); ^{19}F NMR (CDCl_3 , 376 MHz) δ -81.58 (3F, t-t, 1J = 9.9 Hz, 2J = 2.3 Hz), -92.81 - -93.05 (2F, m), -112.89 - -113.15 (2F, m), -122.07 - -122.31 (2H, m), -123.24 - -123.44 (2F, m), -123.89 - -124.05 (2F, m), -126.57 - -126.72 (2H, m); MS (PCI) 454 ($\text{M}^+ + 1$).

4.25 Synthesis of 1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-7-methyl-7-nitro-1-(heptafluoropropoxy)octane $\text{C}_3\text{F}_7\text{O}(\text{CF}_2\text{CF}_2)_3\text{C}(\text{CH}_3)_2\text{NO}_2$ (**IV-C**)

A three-neck round bottom flask under a nitrogen blanket was equipped with a stir bar and a Dean Stark trap. Tetrabutylammonium hydroxide as a 40% solution in water (50 mL, 0.077 moles), 2-nitropropane (7.48 g, 0.084 moles), and benzene (125 mL) were added to the round bottom and the mixture was heated to 85 – 90 °C to azeotropically distill water (30 mL) and benzene (50 mL). The product solution was then cooled to room temperature and used immediately in the next step.

$\text{C}_3\text{F}_7\text{O}(\text{CF}_2\text{CF}_2)_3\text{I}$ (42.84 g, 0.07 moles) was added dropwise at room temperature to the solution of tetrabutylammonium nitropropanide (22.77 g, 0.077 moles) described above. An exotherm to 68 °C was noted. Following the addition, the reaction was stirred overnight at room temperature. Ether (200 mL)

was added and the salt byproduct was filtered through a fritted funnel. After ether removal the filtrate was distilled under high vacuum to yield 15.32 g (38%) of $\text{C}_3\text{F}_7\text{O}(\text{CF}_2\text{CF}_2)_3\text{C}(\text{CH}_3)_2\text{NO}_2$ as an off-white waxy solid. b.p. 52 - 53 °C at 0.2 mmHg; ^1H NMR (CDCl_3 , 400 MHz) δ 1.79 (6H, t, J = 1.2 Hz); ^{19}F NMR (CDCl_3 , 376 MHz) δ -81.12 (3F, t, J = 7.2 Hz), -83.61 - -83.77 (2F, m), -84.88 - 85.04 (2F, m), -115.68 - -115.92 (2F, m), -84.54 - -84.69 (2F, m), -118.68 - -118.90 (2F, m), -122.19 - -122.46 (2F, m), -122.62 - -122.86 (2F, m), -125.98 - -126.17 (2F, m), -130.58 - -130.62 (2F, m); MS (PCI) 572 ($\text{M}^+ - \text{H}$); $\text{C}_{12}\text{F}_{19}\text{H}_6\text{NO}_3$ (573.14) Calc. C 25.15 H 1.06 N 2.44; Found C 28.13 H 1.72 N 2.68. Although this compound did not provide satisfactory elemental analysis result, it was successfully used in the subsequent step.

4.26 Synthesis of 3,3,4,4-tetrafluoro-4-(heptafluoropropoxy)butan-1-amine hydrochloride [$\text{C}_3\text{F}_7\text{OCF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{NH}_3$][Cl] (**I-D**)

A three-neck round bottom flask under nitrogen was charged with $\text{C}_3\text{F}_7\text{OCF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{N}_3$ (35.0 g, 0.0986 mol), 42.5% Raney Ni solution in water (0.72 g, 0.012 mol) and 30 mL of water. Hydrazine monohydrate (7.39 g, 0.148 mol) was added dropwise to the reaction flask in order to prevent the reaction temperature from rising above 40 °C. The reaction was slowly heated to 60 °C and held there for 6 hours. Upon cooling to room temperature the organic layer was separated, dissolved in 150 mL of diethyl ether, and washed with DI water (4 x 50mL). The organic layer was charged into a 250 mL 3-neck round bottom flask and 12 M HCl was added (13 mL, 0.15 mol) dropwise, with ice cooling, over a period of 30 minutes. Cyclohexane (50mL) was added to the reaction flask to promote precipitation of product. The solid precipitate was collected by vacuum filtration and washed with cyclohexane (5 x 100 mL), and subsequently with ether (5 x 50mL) to give 21.65 g (60 %) of $\text{C}_3\text{F}_7\text{OCF}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{NH}_3^+\text{Cl}^-$ (**I-D**) as a colorless solid. m.p. 206 - 209 °C; ^1H NMR (D_2O , 400 MHz) δ 3.47 (2H, t, J = 7.2 Hz), 2.73 (2H, t-t, 1J = 18.3 Hz, 2J = 7.1 Hz); ^{19}F NMR (D_2O , 376 MHz) δ -83.58 (3F, t-t, 1J = 7.1 Hz), -86.73 - -86.89 (2H, m), -90.28 - -90.38 (2F, m), -120.06 (2F,

t, J= 17.8 Hz), -132.15 - -132.18 (2F, m); C₇H₇F₁₁ONCl (365.00) Calc. C 23.07 H 1.79; Found C 23.01 H 1.93.

The synthesis of compound **II-D**, **III-D** **V-D** to **X-D** were performed in a similar manner and the experimental details can be found in supplementary data.

4.27 3,3,4,4,5,5,6,6-octafluoro-6-(heptafluoropropoxy)hexan-1-amine hydrochloride [C₃F₇O(CF₂CF₂)₂CH₂CH₂NH₃][Cl] (**II-D**) m.p.: 220 – 227 °C; ¹H NMR (CD₃OD, 400 MHz) δ 3.39 - 3.37 (2H, m), 2.73 (2H, t-t, ¹J = 18.7 Hz, ²J = 7.4 Hz); ¹⁹F NMR (CD₃OD, 376 MHz) δ -85.18 (3F, t, J = 7.3 Hz), -86.76 - -86.92 (2F, m), -87.79 - -87.94 (2F, m), -117.54 - -117.77 (2H, m), -127.15 - -127.30 (2F, s), -128.76 - -128.90 (2F, m), -133.55 - -133.57 (2H, m); C₉H₇F₁₅ONCl (465.58) Calc. C 23.07 H 1.37; Found C 23.22 H 1.52.

4.28 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-8-(heptafluoropropoxy)octan-1-amine hydrochloride [C₃F₇O(CF₂CF₂)₃CH₂CH₂NH₃][Cl] (**III-D**) m.p. 216 - 228 °C; ¹H NMR (CD₃OD, 400 MHz) δ 3.39 (2H, t, J = 7.2 Hz), 2.76 (2H, t-t, ¹J = 18.6 Hz, ²J = 7.6 Hz); ¹⁹F NMR (CD₃OD, 376 MHz) δ -83.30 (3F, t, J = 7.4 Hz), -85.82 - -85.98 (2F, m), -84.56 - -84.73 (2F, m), -115.39 - -115.63 (2F, m), -123.09 - -123.35 (2F, m), -123.54 - -123.75 (2F, m), -124.78 - -124.97 (2F, m), -126.90 - -127.09 (2F, m), -131.62 - 131.65 (2F, m); C₁₁H₇F₁₉ONCl (565.59) Calc. C 23.86 H 0.87; Found C 23.36 H 1.25.

4.29 Synthesis of 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-2-methyl-8-(heptafluoropropoxy)octan-2-amine hydrochloride [C₃F₇O(CF₂CF₂)₃C(CH₃)₂NH₃][Cl] (**IV-D**)

C₃F₇O(CF₂CF₂)₃C(CH₃)₂NO₂ (30 g, 0.052 moles), 10% palladium on carbon catalyst (4 g), and ethanol (200 mL) was charged into vessel and then pressurized with 1000 psi of hydrogen. The vessel was heated at 80 °C for 16 hours. The crude product was gravity filtered twice to remove the remaining

catalyst to yield a green filtrate. 12M HCl (13 mL, 0.156 moles) was slowly added to the filtrate. The solvent was removed through rotary evaporation yielding a yellow powder. The powder was further dried using a high vacuum pump and treated with 1N KOH (120 mL). The solution was transferred into a separatory funnel, and the organic layer was removed. The basic layer was extracted twice with 50 mL of ether. The organic layers were combined and gently washed with water (20 mL) to prevent emulsification. The organic layer was dried with magnesium sulfate. The solvent was removed and the product was distilled under vacuum to yield a colorless liquid distillate (21.01 g, 0.037 moles) of $\text{C}_3\text{F}_7\text{O}(\text{CF}_2\text{CF}_2)_3\text{C}(\text{CH}_3)_2\text{NH}_2$ b.p.: 85-87 °C at 12 mmHg. The distillate was dissolved in 100 mL of ethanol and the solution was treated with a ten molar excess of 12M HCl (9.2 mL, 0.33 moles). The ethanol was removed through rotary evaporation yielding 20.80 g (69%) of $[\text{C}_3\text{F}_7\text{O}(\text{CF}_2\text{CF}_2)_3\text{C}(\text{CH}_3)_2\text{NH}_3][\text{Cl}]$ (**IV-D**) as a colorless powder. m.p. 165 - 167°C; ^1H NMR (CD_3OD , 400 MHz) δ 1.68 - 1.66 (6H, m); ^{19}F NMR (CD_3OD , 376 MHz) δ -83.22 (3F, t, $J = 7.2$ Hz), -84.47 - -84.67 (2F, m), -85.74 - -85.91 (2F, m), -119.73 - -120.01 (2F, m), -120.20 - -120.47 (2F, m), -122.78 - -123.10 (2F, m), -123.25 - -123.51 (2F, m), -126.80 - -126.91 (2F, m), -131.56 (2F, s); $\text{C}_{12}\text{F}_{19}\text{H}_9\text{NOCl}$ (579.62) Calc. C 24.94 H 1.47 N 2.39; Found C 24.87 H 1.57 N 2.42.

4.30 3,3,4,4,5,5,6,6-octafluoro-6-(pentafluoroethoxy)hexan-1-amine hydrochloride $\text{C}_2\text{F}_5\text{O}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{CH}_2\text{NH}_3[\text{Cl}]$ (**V-D**) m.p. 235 – 239 °C; ^1H NMR (CD_3OD , 400 MHz) δ 3.31 (2H, t, $J = 7.6$ Hz), 2.69 (2H, t-t, $^1J = 18.4$ Hz, $^2J = 7.5$ Hz); ^{19}F NMR (CD_3OD , 376 MHz) δ -84.96 - -85.12 (2F, m), -88.86 - -88.88 (3F, m), -90.07 - -90.17 (2F, m), -115.56 - -115.78 (2F, m), -125.18 - -125.33 (2F, m), -126.86 - -127.00 (2F, m); $\text{C}_8\text{H}_7\text{F}_{13}\text{ONCl}$ (415.57) Calc. C 23.01 H 1.53; Found C 23.12 H 1.70.

4.31 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-8-(pentafluoroethoxy)octan-1-amine hydrochloride $[\text{C}_2\text{F}_5\text{O}(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{NH}_3][\text{Cl}]$ (**VI-D**) m.p. 242 – 251 °C; ^1H NMR (CD_3OD , 400 MHz) δ 3.32 (2H, t, $J = 7.2$ Hz), 2.67 (2H, t-t, $^1J = 18.8$ Hz, 2J

= 7.4 Hz); ^{19}F NMR (CD_3OD , 376 MHz) δ -86.63 - -86.81 (2F, m), -90.79 - -90.84 (3F, m), -91.98 - -92.10 (2F, m), -117.22 - -117.65 (2F, m), -124.85 - -125.33 (2F, m), -125.47 - -125.79 (2F, m), -126.64 - -127.03 (2F, m), -128.79 - -129.24 (2F, m); $\text{C}_{10}\text{H}_7\text{F}_{17}\text{ONCl}$ (515.59) Calc. C 23.28 H 1.20; Found C 23.30 H 1.37.

4.32 3,3,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluorodecan-1-amine hydrochloride [$\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{NH}_3$][Cl] (**VII-D**) m.p. 235 - 240 °C; ^1H NMR (D_2O , 400 MHz) δ 3.50 (2H, t, J = 7.1 Hz), 2.79 (2H, t-t, 1J = 18.7 Hz, 2J = 7.2 Hz); ^{19}F NMR (D_2O , 376 MHz) δ -81.18 (3F, t-t, 1J = 9.9 Hz, 2J = 2.8 Hz), -113.96 - -114.18 (2F, m), -122.16 - -122.35 (2F, m), -123.10 - -123.33 (2F, m), -124.05 (2F, s), -126.32 - -126.46 (2F, m); $\text{C}_8\text{H}_7\text{F}_{13}\text{NCl}$ (399.57) Calc. C 23.85 H 1.65; Found C 24.05 H 1.77.

4.33 5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-N-methyldecan-1-amine hydrochloride [$\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_3$][Cl] (**VIII-D**) m.p. 229 - 232 °C; ^1H NMR (CD_3OD , 400 MHz) δ 2.98 (2H, t, J = 6.8 Hz), 2.26 (2H, t-t, 1J = 19.0 Hz, 2J = 7.9 Hz), 1.83 - 1.67 (4H, m); ^{19}F NMR (CD_3OD , 376 MHz) δ -82.89 (3F, t-t, 1J = 10.3 Hz, 2J = 2.4 Hz), -115.82 - -116.07 (2F, m), -123.28 - -123.57 (2F, m), -124.27 - -124.54 (2F, m), -124.88 - -125.09 (2F, m), -127.74 - -127.96 (2F, m); $\text{C}_{10}\text{H}_{11}\text{F}_{13}\text{NCl}$ (427.63) Calc. C 28.08 H 1.81; Found C 28.06 H 1.93.

4.34 3,3,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-N-methyldecan-1-amine hydrochloride [$\text{C}_6\text{F}_{13}\text{CH}_2\text{CF}_2\text{CH}_2\text{CH}_2\text{NH}_3$][Cl] (**X-D**) m.p. sublime at 170 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 3.23 (2H, t, J = 7.3 Hz), 3.18 - 3.03 (2H, m), 2.50 (2H, t-t, 1J = 17.8 Hz, 2J = 7.5 Hz); ^{19}F NMR (CDCl_3 , 376 MHz) δ -82.84 (3F, t-t, 1J = 10.3 Hz, 2J = 2.5 Hz), -96.81 - -97.07 (2F, m), -113.42 - -113.64 (2F, m), -123.02 - -123.28 (2F, m), -124.10 - -124.38 (2F, m), -124.61 - -124.71 (2H, s), -127.60 - -127.75 (2F, m). $\text{C}_{10}\text{F}_{15}\text{H}_9\text{NCl}$ (463.61) Calc. C 25.91 H 1.96 N 3.02; Found C 25.88 H 1.86 N 3.04.

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